

**Chemistry and Transport of Nitrogen Oxides on the Western Slopes of the
Sierra Nevada Mountains: Implications for Lake Tahoe**

Final report: Interagency Agreement #02-331

Prepared for

California Air Resources Board

Research Division

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July 1, 2004

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I. Introduction

Over the last 35 years, visibility into the depths of Lake Tahoe has decreased from 30 to 20 meters. Research suggests that a large part of this decline in water clarity is associated with increases both in fine sediment particles and in nutrient availability to microorganisms within the lake (Jassby et al. 1999). Estimates suggest that the productivity of microorganisms in the Lake was nitrogen limited in the late 1960s and 1970s, but that it is now primarily phosphorous limited (Goldman et al. 1993). Atmospheric deposition of phosphorus and nitrogen is thought to be an important mechanism for nutrient input to the lake, and direct deposition to the Lake has been estimated to account for about 50% of the combined annual loading of these nutrients (Jassby et al. 1994). Additionally, atmospheric deposition to surfaces within the Lake Tahoe basin may substantially contribute to runoff into the Lake. In this review, we describe current knowledge of the concentrations of nitrogen oxides and their transport along the western slopes of the Sierra Nevada. We estimate the potential for precursors of particulate nitrates and nitric acid emitted in the Central Valley to reach the Lake Tahoe Air Basin. We also comment on transport of non-reactive nitrogen species such as ammonia.

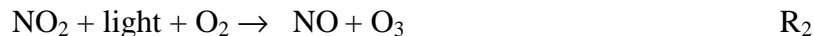
Most deposition of bioavailable nitrogen from the atmosphere occurs in the form of nitric acid (HNO_3), ammonia (NH_3), ammonium (NH_4^+), or nitrate (NO_3^-). However, many additional nitrogen-containing chemicals are found in the atmosphere and most of them are removed by deposition, although more slowly than HNO_3 . Sources of atmospheric nitrogen in the Lake Tahoe Air Basin include in-basin sources, including those associated with stationary and mobile combustion, with fertilizer application, and with redeposition of biogenic emissions from the local ecosystems. A similar mixture of sources contribute to nitrogen transported from outside

the basin: there is a global background of concentrations of nitrogen oxides and $\text{NH}_3/\text{NH}_4^+$ that sets a lower limit on the bioavailable nitrogen; emissions from urban and farming centers to the west of the Lake add to this background; mobile sources that travel between those centers and the Tahoe basin are also a significant source of emissions; and finally natural emissions from the ecosystems located between the Central Valley and Lake Tahoe are also sources of nitrogen-containing compounds.

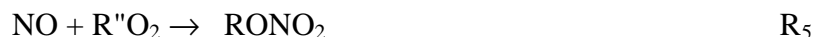
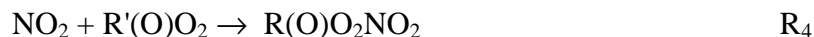
While several studies have addressed the potential transport of pollutants from the Central Valley to more remote locations, many of them focus on individual events and, especially in the case of ozone studies, extreme events that lead to air quality violations. In relation to nitrogen deposition, the cumulative effects of transport on seasonal and annual timescales need to be considered. Short term studies can be used to identify possible transport patterns or occurrences but long term observations are required for an accurate representation of the overall contribution of transport to the deposition of N within the Tahoe Basin. Sections II and III of this report deal with dry deposition of reactive nitrogen, which refers to the direct transfer of gas and particle phase species to the Earth's surface without the aid of precipitation. Section IV examines the role of wet deposition, in which airborne species are transferred to the surface in aqueous form, such as rain, snow or fog. Estimates in Jassby et al (1994) and Tarnay et al (2001) suggest that wet deposition contributes one half to two thirds of direct atmospheric N deposition to the surface of Lake Tahoe.

II. Chemistry of Nitrogen Oxides

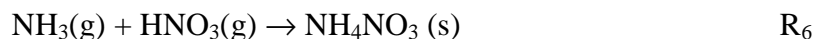
Nitric oxide (NO) is the primary reactive nitrogen compound emitted by biological activity and as a byproduct of combustion. Once emitted, NO rapidly (~100 seconds) interconverts with NO₂



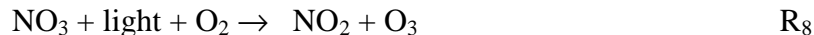
Collectively, NO and NO₂ are referred to as NO_x and the sum of NO_x and all higher oxides of nitrogen is referred to as NO_y. Higher oxides of nitrogen are formed in reactions of the radicals OH, HO₂ and RO₂ with NO and NO₂, principally:



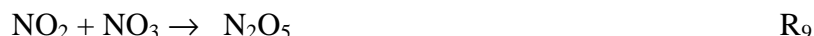
These reaction products have very different properties. Peroxynitrates are thermally unstable and form a reservoir for NO_x, in which the partitioning depends on the ambient temperature. HNO₃ and hydroxyalkyl nitrates (R'' = ROH) are very water soluble while the peroxy nitrate and alkyl nitrate products of R₄ and R₅ are only weakly water soluble. As a result of its solubility, HNO₃ is rapidly (on a time scale of hours within the planetary boundary layer) removed from the atmosphere by deposition to the Earth's surface and/or rapidly scavenged in water-rich aerosols, which then deposit to the Earth's surface. Less is known about the deposition rates of hydroxyalkyl nitrates but measurements of their Henry's law solubilities strongly suggest that their deposition rates should be similarly to that of HNO₃. Deposition of NO₂, alkyl nitrates, and peroxynitrates are a factor of 10 slower than deposition of HNO₃ (Wesely and Hicks 2000). The most abundant peroxynitrate, PAN, is a known phytotoxin at the concentrations (~5 ppb) encountered immediately downwind of Sacramento (Cape 2003). HNO₃ also reacts with NH₃ in the gas phase or within particles to produce an ammonium nitrate salt: NH₄NO₃. The equilibrium is shifted toward ammonium nitrate aerosol at low temperature and high relative humidity, and the particles may have different atmospheric lifetimes than gas phase HNO₃ (Seinfeld and Pandis 1998).



The nitrate radical, NO₃, is formed from the oxidation of NO₂ by O₃ (R₇). However, NO₃ is rapidly destroyed by sunlight (R₈).



At night, when the very rapid photolysis of NO₃ (R₈) is not occurring, NO₃ accumulates and then reacts to form N₂O₅ via R₉:



HONO is also rapidly photolyzed during the day and accumulates at night as a result of mechanisms that are poorly understood, but appear to be equivalent to:



N₂O₅ and HONO are highly reactive with and soluble in water and are likely removed from the atmosphere on contact with most surfaces. The role of these important nighttime compounds in redistributing reactive nitrogen is not well understood.

III. Transport

Transport of nitrogen oxides from the Central Valley and the western slopes of the Sierra Nevada to Lake Tahoe can result from processes including: a) direct transport within the planetary boundary layer (PBL), b) direct transport above the PBL; and c) accumulation of pollutants in a regional background (Figure 1). The first two of these mechanisms operate on a timescale of several (5-20 hours). Accumulation of pollutants in a regional background and subsequent transport to Tahoe operates on longer timescales (multi-day). All three of these mechanisms are expected to operate, though to differing extents, every day. Research also suggests that biomass burning may be a significant source of atmospheric nitrogen and phosphorus in the Lake Tahoe Basin (Zhang et al. 2002) and it is well known that biomass fires can be significant sources of longer lived pollutants such as CO on a continental scale (Novelli et al. 2003). Fires are episodic in nature, the extent to which their emissions will impact the Basin rests on their frequency, intensity, and proximity to Tahoe.

The overall impact of remote sources of atmospheric reactive nitrogen on Lake Tahoe depends on the appropriately weighted combination of all of the above pathways. In the summer, the prevailing wind flow is from the west at all altitudes more than 2000 m above the surface. During the day, heating of the western Sierra Nevada generates upslope winds that transport air from the valley floor into the mountains, regardless of the dominant flow regime within the Central Valley itself (Zaremba and Carroll 1999). In winter, significant periods of high pressure in the region cause inland valleys and basins to fill with cold air leading to low mixing heights and weak winds. Local pollutants tend to accumulate and long range transport of emissions is less likely. While the pattern of upslope/downslope flow is observed on some winter days, the shorter periods of daylight mean that upslope flow persists for a much smaller fraction of the day. Figure 2 shows the summer and winter patterns of upslope/downslope flow at the University of California's Blodgett Forest Research Station (UC-BFRS, 1400 m ASL).

Figure 1 depicts the transport pathways of pollutants originating in the Central Valley and being advected toward the Tahoe Basin. The dotted line is used to suggest the mixing height or upper edge of the planetary boundary layer. Urban emissions may be transported within the PBL along path 1 or lofted above and transported in the free troposphere by path 2,3. If westerly flow is strong enough or persists long enough during a given day, it may reach the Tahoe Basin. Arrow 4 is dotted to emphasize that it is unclear how often conditions directly transport an air parcel originating in the valley this far east before the winds turn around at night. While pollutants may not be directly transported to Tahoe within the mixed layer, emissions into an air mass that sloshes up and down the slope of the Sierra every day may increase the regional background over time, eventually contributing to elevated reactive nitrogen in air that reaches the Tahoe Basin. A detailed understanding of how air within the Tahoe Basin mixes (arrow 5) is also necessary to assess the influence of remote nitrogen sources. Pollutants transported aloft via pathway 2,3 will have no effect on Lake Tahoe unless they enter the mixed layer above the lake, which would permit their eventual deposition. An assessment of the probability of such events is beyond the scope of this review.

IIIa. The urban plume

The daily evolution of the Sacramento urban plume during the summer is remarkably consistent. During the day, terrain driven winds blow steadily from Sacramento into the Sierra Nevada foothills – drawing air into the sparsely populated mountains. During the night, the wind reverses and clears out the mountains replacing the urban plume with the regional background. Observations of atmospheric composition and meteorology show this pattern persists up to at least 1200 m elevation (Carroll and Dixon 2000). Transport of anthropogenic emissions from the Sacramento metropolitan area as a result of this meteorological flow pattern is evident in observations of anthropogenic hydrocarbon, ozone, and nitrogen oxide concentrations at the University of California Blodgett Forest Research Station, which peak in the late afternoon/evening and decrease steadily with the downslope flow during the night. *Van Ooy and Carroll* (1995) measured ozone and local meteorological variables (temperature, wind speed, wind direction, relative humidity, and solar radiation) at six sites along a 400 km north-south transect of the Sierra Nevada foothills (1100 – 1200 m elevation) during the summer of 1992. At the three sites where east-west wind patterns are predominant, as they also are at UC-BFRS, there was a strong correlation between wind direction and ozone concentrations. At these sites, there was a regular diurnal pattern with ozone concentrations peaking at 15:00 to 17:00 PST (Pacific Standard Time) and reaching a minimum at 7:00 PST. At the other three sites where north-south winds were predominant, the diurnal variation in ozone was small. The sites with east-west wind patterns had higher peak ozone abundances and violated the one hour state ozone standard of 90 ppb up to 40% more often than the sites with predominantly north-south winds indicating sites with east-west wind patterns such as UC-BFRS represent a maximum effect of transport. The major climate variables controlling transport in the region (temperature, sunlight, precipitation, relative humidity, and wind) as measured in Sacramento have been nearly constant for 20 years (1980 to 1999) (Figure 3). Thus emissions in the Central Valley should have been transported with equal efficiency throughout this 20-year period.

These analyses suggest the plume travelling into the foothills of the Sierra from the Valley serves as a mesoscale (~100 km) daytime flow reactor that can be characterized as a Lagrangian air parcel transported from the Valley into the Sierra Nevada. *Dillon et al.* (2002) used comprehensive (ozone, speciated nitrogen oxides, speciated anthropogenic and biogenic hydrocarbons, and meteorology) and extensive observations (spanning the years 1997 to 2002) at Folsom, California and five hours downwind at the UC – Blodgett Forest Research Station to

evaluate transport from Sacramento into the mid-Sierra during the summer (Figure 4). The observations at Folsom effectively integrate all of the emissions to the west. *Dillon et al.* (2002) established that a Lagrangian analysis captures the essential features of the chemistry and transport and fit the parameters of a Lagrangian model to the observations. Comparison of ozone and meteorological observations to the north of UC-BFRS at Blue Canyon and to the south at Sly Park support the suggestion that the observations and the model analysis are regionally representative *Dillon et al.* (2002).

Measurements of NO_y and individual NO_y species at UC-BFRS (1998-present) demonstrate pronounced seasonal variability (Day et al. 2002) (Figure 5). The Lagrangian model has only been applied to summer time conditions when upslope transport is expected to be at a maximum. To obtain an annually complete picture, other approaches are required to interpret the reactive nitrogen measurements because of different source distributions, and more importantly, very different meteorological conditions.

Mixing

Parameters in the model described by *Dillon et al.* (2002) include mixing of the urban plume with the regional background, chemical processing, emission and deposition. Mixing of the plume occurs on a time scale of 4 hours during daytime upslope flow. Treating NO_y as a conserved quantity in calculations represents an upper limit to the contribution of urban NO_y in the Sierra Nevada since chemical factors also act to reduce NO_y . Based on mixing alone, by the time the plume arrives at UC-BFRS, 5 hours downwind from the suburbs of Sacramento, the urban emissions are diluted to 28% of their initial concentration by mixing with the background. If we extrapolate these results to Tahoe, which is another 4 hours downwind, the urban portion of the concentrations would be 10% of their initial values. In the summer, the regional background in the area is estimated to be 1.9 ppb, and daytime NO_y mixing ratios in the downwind suburbs of Sacramento are 7 ppb, thus 5.1 ppb is the direct result of local emissions. Based on mixing alone, after five hours of transit the concentration of NO_y at UC-BFRS would be 3.4 ppb (1.5 ppb from the plume, and 1.9 from the regional background). Extrapolating to Lake Tahoe, the concentration of NO_y would be 2.4 (0.5 ppb from the plume, and 1.9 from the regional background). Observations by *Carroll et al.* (2002) along a transect at 2000 m suggest the urban plume usually stops there and does not progress across the pass into the Lake region,

indicating that direct transport of inorganic nitrogen from the Central Valley is likely smaller than this estimate.

HNO₃ formation and deposition

Chemical production of HNO₃ followed by rapid deposition removes NO_y reducing the urban contribution below the estimate given above for mixing alone. *Dillon et al.* (2002) determined that the effective OH mixing ratio that acts over the 5-hour transport time to Blodgett Forest is about 1.4×10^7 molecules/cm³ or (0.6 ppt). NO₂ reacts rapidly with OH to form HNO₃ ($k \sim 9 \times 10^{-12} \text{ s}^{-1} \text{ cm}^3/\text{molec}$) and in the absence of other reactions of NO₂, approximately 90% of the suburban NO₂ would be converted to HNO₃ prior to reaching UC-BFRS. HNO₃ is deposited on a time scale set by the ratio of the deposition velocity to the boundary layer height. Using literature estimates for the deposition velocity (0.035 m/s) (Hanson and Lindberg 1991) and the boundary layer height (800 m) (Seaman et al. 1995), results in a lifetime of 6.3 hours. Thus, about 50% of the HNO₃ formed during the transit to UC-BFRS is deposited along the way and about 85% is deposited before it gets to the Tahoe basin. *Day et al.* (2002) provide analysis of the daily cycle of HNO₃ that suggests this estimate of the HNO₃ lifetime is too long (perhaps because the deposition velocity is closer to 0.05 m/s). During the daytime, the HNO₃ concentration is observed to be nearly in a chemical stationary state with a production term characterized by R₃ and loss to deposition. This would not be the case if the time scale for production and deposition were much longer than 3 hours. This result implies that more than 70% of the HNO₃ formed during transit from Sacramento to Tahoe is deposited along the western slope of the Sierra Nevada. This short lifetime suggests that attention be focused on the controls over NO₂ mixing ratios in the Tahoe basin (or anywhere else where dry HNO₃ deposition is a potential problem). The deposition velocity of ammonia is similar to that of HNO₃; thus, we can make similar assumptions about its lifetime in the plume. Since NH₃ is a primary pollutant, its concentration should start decreasing immediately as the air mass moves away from the emission source. Under humid conditions, the formation of NH₄NO₃ particles could prolong the lifetime of these forms of inorganic nitrogen. Warm daytime temperatures in summer favor gas phase species but aerosol may be important in the winter or at night.

Organic Nitrate (RO_xNO_2) Formation

Other photochemical byproducts that act as a sink or reservoir for NO_x include peroxy nitrates and alkyl nitrates formed by the reaction of RO_2 with NO_2 and NO respectively. In the concentration range of NO_x encountered outside urban areas, organic nitrates can be the major sink of NO_x radicals. While HNO_3 forms efficiently under high NO_x conditions, RO_xNO_2 formation becomes more favorable as the NO_x to hydrocarbon ratio decreases. The lower deposition velocity of organic nitrates lengthens their lifetime in the plume but also makes them less efficient as a source of atmospheric nitrogen to the surface. Hydroxy alkyl nitrates are expected to have comparable deposition velocities to HNO_3 , but it is unclear what fraction of organic nitrates these comprise. Peroxy nitrates are thermally unstable and therefore capable of sequestering NO_x under cold conditions and releasing it once temperatures rise. This can be an effective mechanism for transporting reactive nitrogen to distant places. Observations by Day *et al.* (Day et al. 2003) at UC-BFRS show that for many parts of the year, the sum of all organic nitrate species is often the most significant fraction of NO_y in the plume by the time it reaches the site. More needs to be known about the behavior of these species to assess their potential to deliver reactive nitrogen to Lake Tahoe. Note that atmospheric chemists refer to $RONO_2$ and RO_2NO_2 collectively as ‘organic nitrates’; a term that should not be confused with ‘organic nitrogen’, which is used to refer to compounds with a C-N bond. Little is known about the aqueous decomposition of peroxy and alkyl nitrates, and whether their NO_3 group would contribute to nitrate measurements in analysis of lake water or precipitation.

Downwind emissions

The observations and analyses of nitrogen oxides at UC-BFRS indicate that emissions into the urban plume continue after it passes over Folsom. These emissions are large ~0.44 ppb/hr. After the five hours of travel on the way to UC-BFRS, the total emissions are 2.2 ppb, an amount in excess of the background concentration observed at the site and fully 2/3 of the amount observed at the peak of the urban plume. This result strongly implies that transportation along the major highway corridors (50 and 80), contribution from housing beyond the edge of the Sacramento suburbs and direct emissions from the local ecosystems are significant contributors to NO_y in the Sierra. Further research is required to quantify the amount contributed by each of these distinct sources.

Summary of plume transport and chemistry

The above analysis makes use of a continuous long term dataset that allows for the evaluation of statistics. This comprehensive record of meteorology and chemical composition at UC-BFRS is consistent with other observations from the western slope of the Sierras including aircraft measurements, data from Big Hill (1850 m), and short term ozone studies. Using a model that accounts for the combined effects of emissions, chemistry, deposition and dilution which can be tested against an inclusive set of observations allows us to develop an representation of the mean behavior of NO_y species in the region. The influence of the urban plume causes an increase in the typical daytime peak mixing ratio of NO_y at UC-BFRS, which occurs just prior to sunset, to near 3.3 ppb, an amount that is 1.4 ppb above the regional background of 1.9 ppb. For most of the day, the observed mixing ratios are much less than this peak value with a daytime average concentration of about 2.5 ppb (0.6 ppb above the regional background). Thus on an average day at UC-BFRS, the contribution of the urban plume raises the diurnally averaged NO_y by 32% over the background. Assuming the Lagrangian parameters represent transport beyond UC-BFRS, then further dilution and deposition of HNO_3 along the plume's trajectory to the Lake will mean an even lower contribution of NO_y from the urban plume to the Tahoe basin.

At least as important as the total amount of NO_y transported within the plume, is the change in species distribution as the plume evolves. HNO_3 dominates the higher oxides of nitrogen (NO_z) near emission sources of NO_x but is rapidly lost if the air mass remains in contact with the surface. On the other hand, the plume becomes relatively enriched in organic nitrates as it progresses through the day with the sunlight driving hydrocarbon oxidation, creating RO_2 radicals to combine with the NO_x in the plume. These hydrocarbons have both anthropogenic and biogenic sources. If nitrogen oxides emitted in the Valley do reach the Tahoe Basin, it is likely they will make it there in the form of organic nitrates. Production of fine particles ($<2.5 \mu\text{m}$ aerodynamic diameter) containing nitrate may be another mechanism for transporting reactive nitrogen, as this size of aerosol has a substantial lifetime (hours-days) in an air mass.

The direct extrapolation of the plume analysis presented above in order to understand inputs to Lake Tahoe is only accurate if the upslope flow is strong enough and persistent enough to deliver air from the Central Valley to the Tahoe Basin in one day. If an average daytime wind

speed of 3.5 m/s is used, it would be possible for an air mass to leave Sacramento at 10 am and travel 130 km east to the Tahoe Basin by 8 pm that night. Using appropriately timed NO_2 , NO_x , and NO_y observations from monitoring sites along the Sacramento-Tahoe transect in July enables us to examine the evolution of reactive nitrogen in the plume (Figure 6). As described above, as the plume moves away from Sacramento and ages, the abundance of reactive nitrogen decreases as the result of dilution, processing and deposition. However, NO_x observations at South Lake Tahoe are substantially higher than one would expect from an extension of the values at UC-BFRS and Big Hill, suggesting a substantial contribution from local in-basin emission sources.

Limited aircraft measurements of $\text{HNO}_3/\text{NO}_3^-$, $\text{NH}_3/\text{NH}_4^+$, and organic nitrogen in the gas and particle phase have been made in the Tahoe Basin and at low and mid-elevation sites along the western slope of the Sierra Nevada (Zhang et al. 2002). While the abundance of these species is significantly lower in the Basin than on the Western slope of the Sierras, the distribution between the species was found to be similar in all locations. The authors infer from these observations that under summertime meteorological conditions, Central Valley emissions can be a significant source of nitrogen to the basin. However, because the timescale of photochemistry and deposition of the nitrogen oxides is short, we expect the distribution among different classes of NO_y to have strong variations depending on the time of day and proximity to the source, but not necessarily the identity of the source. Further, if the Central Valley was the main source of HNO_3 and NH_3 for all the sites, because Tahoe is further along the transect than the lower elevation sites, one might actually expect a very different N distribution. Additionally, there may be some bias resulting from the timing of the measurements: all the western slope measurements occur between noon and 4 pm while half of the Tahoe Basin measurements are in the morning. These intermittent observations are not sufficient to address the issue of transport from the western slope into the basin.

IIIb. Other transport paths

The typical ground level monitoring network does not effectively characterize air pollution transport aloft. It is possible that air with high concentrations of nitrogen oxides is lofted well above the surface in the Central Valley and then transported to the east without further contact with the surface until arriving in the high Sierra or the Tahoe basin itself. Air that

does not contact the ground would not be subject to the same deposition losses as that within the planetary boundary layer. However, there is no evidence to suggest that this is a mechanism for persistent and effective transport. Although there are some aircraft and ground-based data that suggest high concentrations of pollutants can be trapped above the nocturnal boundary layer in the Sacramento region (Carroll and Dixon 2002), the same aircraft data show that the plume does not travel east into the Sierra Nevada beyond the ridges at about 2000 m ASL. Aircraft observations made above the Lake suggested that conditions of neutral stratification over the lake promote vertical mixing, which would enable pollutants passing over the lake at high altitudes to mix downwards, but would also result in significant dilution. A more quantitative approach is required to assess the probability that air from the west passes over the Sierra crest to Lake Tahoe and penetrates the mixed layer over the lake surface, thus permitting dry deposition of atmospheric nitrogen from sources upwind of the basin.

IIIc. The regional background

The background concentrations of NO_y observed at UC-BFRS, which evidence suggests is widespread in the foothills of the Sierra Nevada, is likely the major component of nitrogen oxides that enter the Tahoe basin from the west. On days when the urban plume does not reach Lake Tahoe, the reactive nitrogen contained within it may remain in the Sierra and contribute to increased background levels of atmospheric nitrogen and enhanced deposition. However, nighttime chemistry may remove nitrogen oxides before the following day. The broader influence of the emissions from Sacramento and the Central Valley depend on the synoptic weather patterns and the distribution of reactive nitrogen among its constituent compounds. In the summer, net air flow is from the west and emissions from the Central Valley can accumulate along the western slope of the Sierra and ultimately affect the Tahoe Basin. In the winter, observations at UC-BFRS and at Camino, along Highway 50, suggest that the net air flow at the surface is actually from the east (Figure 7). This is consistent with much lower background values of NO_y during the colder season, and suggests that emissions from the west do not undergo net transport toward Tahoe in the surface layer during the winter. Observations to date do not provide an adequate explanation for the observed background and further research is needed.

IIIId. Burning

Forest fires and biomass burning are recognized to have significant effects on nearby ecosystems. Efforts have been made to characterize and quantify the pyrogenic emissions from various fuel sources (e.g., Andreae and Merlet 2001). Studies of biomass burning plumes have identified elevated levels of many reactive nitrogen species and observed a change in NO_y partitioning as the plume aged (Mauzerall et al. 1998). Another study noted an increase in nitrate-containing particles as the smoke aged over the first hour (Hobbs et al. 2003). Zhang et al. (2002) intercepted a forest fire plume during flights over the northern edge of the Tahoe Basin and observed elevated concentrations of reactive nitrogen 35 km downwind of the fire. The observations also demonstrate an enrichment in organic nitrogen in the particulate phase, consistent with the nitrogen partitioning observed another day in slightly smoky air over Lake Tahoe. Burning may not only liberate additional nitrogen oxides into the atmosphere, but also lead to a redistribution of the species, affecting the deposition rate of nitrogen to the lake. In order to assess the contribution of burning events to the nitrogen oxides in the Tahoe Basin, a detailed inventory of burning frequency, intensity and location is required, in conjunction with detailed knowledge of temperature and wind patterns.

IV. Wet Deposition of Nitrogen within the Tahoe Basin

Few studies have addressed wet deposition, which occurs mainly in the winter, and at high elevations is generally the result of snow rather than rain. The contribution of wet deposition to total N deposition within the Tahoe Basin cannot currently be quantified, because no studies have measured gas and aerosol phase nitrogen in the atmosphere and in precipitation on a year-round basis. Observations of the NO_3^- and NH_4^+ content of precipitation in the Tahoe Basin by Jassby et al. (1994) allow us to estimate the relative contributions of in-basin nitrogen sources to the wet deposition of nitrogen to the surface of Lake Tahoe. Jassby et al. record dry and wet N deposition data for a station at Ward Creek, and an east-west transect across the lake. They observe that NH_4^+ and NO_3^- are the dominant forms of N in wet deposition, and they estimate that the average deposition across the basin is half the deposition at Ward Creek. This estimate is supported by measurements over several years by Melack et al. (1997) of nearby

alpine snowpacks which found 2240-5370 $\mu\text{mol}/\text{m}^2$ NO_3^- and 2160 to 5840 $\mu\text{mol}/\text{m}^2$ NH_4^+ prior to spring snowmelt. They note that much of the variability is derived from the timing of the precipitation events.

Data from in Jassby et al. (i.e., Tables 1 & 7) was used to compile the table below, which documents the average precipitation each year and the average amounts of NO_3^- and NH_4^+ found in the precipitation. The difference is the excess of nitrate, which could result from wet deposition of gas phase HNO_3 or wet deposition of other nitrate salts such as $\text{Ca}(\text{NO}_3)_2$ in the precipitation.

Table 1. Precipitation Volume and Inorganic Nitrogen Content for a Tahoe Basin Site

Year	Precipitation (m)	NO_3^- ($\mu\text{mol}/\text{m}^2$ year)*	NH_4^+ ($\mu\text{mol}/\text{m}^2$ year)*	Difference ($\mu\text{mol}/\text{m}^2$ year)	Ratio
1989	1.20	3650	3176	474	1.15
1990	0.785	3960	3650	310	1.08
1991	0.75	2573	2080	493	1.24
1992	0.653	2354	1790	564	1.32

*multiply ($\mu\text{mol}/\text{m}^2$ day) at Ward Creek by 365 days and divide by 2 for basin average

If we assume that all the nitrogen deposited at the Lake was contained in the precipitation before it entered the basin, this would require snow or rain with 3.0, 5.4, 3.4, 3.6 μM concentrations of NO_3^- and 2.6, 4.6, 2.7, and 2.7 μM NH_4^+ . This is similar to precipitation falling over the 1200-1800 m elevation range in Washington's Cascade mountains, which had an average wintertime nitrate concentration of 3.2 μM (Duncan et al. 1986). Comparison of these concentrations to remote sites allows us to estimate the effect of upwind or local emissions. Between 1993-1996, precipitation over a montane forest in Hawaii (Heath and Huebert 1999) had an average $[\text{NH}_4\text{NO}_3]$ of 1.5 μM , and $\text{NO}_3^-:\text{NH}_4^+$ ratios ranging between 1.0 and 1.4, similar to Tahoe. In another study, over Bermuda in 2000, nitrate concentrations ranged between 1.4 μM for airmasses originating over the ocean up to 16.8 μM for back-trajectories which originated over continental USA (Hastings et al. 2003). Precipitation that develops over clean marine areas has NH_4NO_3 below 2 μM so it is likely that upwind or in-basin anthropogenic emissions contribute partly to the N content of precipitation in the basin.

To estimate the potential contribution of in-basin atmospheric nitrogen to wet deposition, we consider the wintertime meteorology and chemistry. Over 90% of precipitation over Lake Tahoe falls between October and May, when the average maximum and minimum temperatures are below 10 °C and 0 °C. Under these conditions and at high relative humidity, gas phase HNO_3 and NH_3 partition strongly into the aerosol phase. NH_4NO_3 particles smaller than 2.5 μm have relatively slow deposition velocities ($< 1 \text{ cm/s}$) and can persist for days in the atmosphere. Analysis of IMPROVE data for Bliss and South Lake Tahoe show that NH_4NO_3 at the two sites are almost equal during summer, but South Lake Tahoe has substantially more nitrate aerosol than Bliss from October through April. A possible explanation for this wintertime gradient is that a combination of low mixing heights and frequent precipitation during the winter prevents the aerosol from mixing throughout the basin and results in higher concentrations closer to sources of NO_x . Because of the low temperatures, and the fact that NO_3^- is consistently higher than NH_4^+ , we can assume that gas phase NH_3 is negligible during the winter months in the basin, and we assume that NH_4^+ is equimolar to NH_4NO_3 . An upper estimate of 500 ng/m^3 is reasonable for both aerosol NH_4NO_3 (0.16 ppb) and gas phase HNO_3 (0.20 ppb) averaged over the Lake Tahoe Basin. If the atmosphere is well-mixed to a height of 1 km above the lake surface, and the precipitation falls through this 1 km, completely scrubbing the aerosol and gas phase concentrations of 500 ng/m^3 NH_4NO_3 and HNO_3 , then every m^2 of lake surface would receive 6.25 μmol of NH_4NO_3 , and 7.9 μmol of HNO_3 . As an upper limit, if 50 such precipitation events were possible in a year, with the atmosphere recovering its concentrations of NH_4NO_3 and HNO_3 between each event, then 300 $\mu\text{mol/m}^2$ of NH_4NO_3 and an additional 400 $\mu\text{mol/m}^2$ of HNO_3 could be deposited annually. This conservative estimate contributes only 10-20 % of the observed wet deposition of nitrogen in the basin. The difference between the observed annual rates of wet N deposition and the amount contributed by in-basin inorganic nitrogen and ‘clean’ rain can likely be attributed to incorporation of atmospheric nitrogen into the cloud chemistry on the path from a meteorological marine front, through coastal and urban areas, and finally ending in alpine precipitation. A recent modeling study integrating multiphase chemistry and microphysics has shown that during cloud and precipitation formation pernitric acid is taken up by the water and converted to nitrate (Leriche et al. 2003). Because NO_2 is in thermal equilibrium with pernitric acid, this results in a mechanism whereby upwind sources of atmospheric NO_x can be efficiently transferred into precipitation to form soluble nitrate. It

should be noted that winter precipitation in the Tahoe Basin has only twice the nitrate observed at remote locations. whereas many sites in Asia, Europe, and the United States have nitrate levels an order of magnitude higher. Thus, the source of the difference between wet N deposition and the amount contributed by in-basin inorganic nitrogen should be considered global in character and not particular regional influences just west of Tahoe.

V. Summary

In addition to local sources of reactive nitrogen to the Tahoe Basin, other potential upwind sources include emissions from the Sacramento urban area, industrial and agricultural activity in the Central Valley, transportation along highway corridors, biomass burning and biogenic emissions from ecosystems within the western Sierra Nevada. The ability of these emissions to affect the water quality of Lake Tahoe depends on their chemical processing and on the transport pathways that bring the air toward the Tahoe Basin. Analysis of long term ground level observations suggest that most HNO_3 within the urban plume deposits prior to reaching Lake Tahoe, though organic nitrates may persist. Short-term aircraft studies attempting to identify transport pathways for pollutants have occasionally observed higher concentrations of photochemical products lofted above the mixed layer. Downwind of biomass burning episodes, elevated levels of reactive nitrogen in both the gaseous and particulate phase have been observed [Zhang, 2002]. If these burning events occur within five hours transit time to the Tahoe Basin, they may be capable of delivering additional nitrogen to the atmosphere above the Lake. Our best estimate is that wet deposition (which Jassby (1994) approximates as half the source of N to the lake) derives 50% its nitrogen content from the global background, 10-20% from local in-basin sources and the remainder from other sources, possibly to the west of the basin. More quantitative research is needed to understand the flow dynamics within the Tahoe Basin that would permit better characterization of vertical mixing processes and improve estimates of reactive nitrogen dry deposition to the lake.

VI. Key Research Issues

To ascertain whether reactive nitrogen emissions from upwind air basins contribute to nitrogen deposition in the Lake Tahoe basin, a spatially and temporally comprehensive representation of the atmospheric chemistry and dynamics of the region is required. Nitrogen deposition is a chronic problem, in contrast to extreme events such as exceedances of the O_3 standard, and requires collection and analysis of longterm data sets. The chemical species involved: NO_x , organic nitrates, HNO_3 , NH_3 , and NH_4NO_3 have lifetimes on the order of hours to days, which means that both daily and synoptic weather patterns in the area must be considered. Both gas phase and aerosol species must be measured, and a complete understanding requires consideration of both dry and wet deposition.

There are essentially two linked but separate questions that need to be addressed:

- 1) What is the nitrogen flux to the Tahoe basin and subsequently to the surface of Lake Tahoe?
- 2) What are the sources of the nitrogen species that deposit onto surfaces within the basin?

Answering the first question requires sensitive, high time resolution measurements of meteorological parameters and the above-mentioned species throughout the Lake Tahoe basin, including NO_3^- and NH_4^+ measurements in precipitation during rain/snow events. This will enable quantification of mechanisms for nitrogen transfer to the Lake including both direct atmospheric deposition to the Lake and atmospheric deposition to other basin surfaces followed by runoff with high N-content.

The temporal and spatial variability in this data can be interpreted to give some indication of the sources of reactive nitrogen to the basin. Also, measurements made upwind of the basin can be used as a boundary condition on the total amount of reactive nitrogen available in upwind airmasses before they enter the Lake Tahoe basin. Data collected at sites on the western slope of the Sierra Nevada suggest that the transit time of a boundary layer air mass from Sacramento to Lake Tahoe generally exceeds the period of upslope flow during a summer day. This implies that if upwind reactive nitrogen emissions from urban areas have any impact over Lake Tahoe, then it is through an increase in the regional background. The lifetime of reactive nitrogen is

largely determined by the deposition rates of its constituent members. Organic nitrates and NH_4NO_3 aerosol (PM 2.5) are longest-lived and therefore most likely to persist in the background, but, because of their correspondingly slow deposition rates, they are also the least likely to deposit to the lake surface. Thus, it is easy to imagine a scenario in which the majority of reactive nitrogen in an air mass over Lake Tahoe has its origin in aged Sacramento emissions but the recent in-basin emissions of NO_x , quickly oxidized to HNO_3 , are what actually deposits to the lake surface. This underlines the need to obtain high time resolution, spatially comprehensive observations of all the members of the reactive nitrogen family if the goal is to quantify deposition AND ascertain the source of the deposited nitrogen.

To more quantitatively assess the contribution of in-basin and out-of-basin nitrogen sources it is necessary to improve our understanding of:

- the total amount of atmospheric deposition to the basin, both directly to the lake surface, and to other areas of the basin that capture nitrogen with subsequent transport to the lake
- the relative contributions of wet and dry deposition
- the importance of burning events on the western slope based on emissions and meteorology
- the deposition rates of all atmospheric forms of N, including HNO_3 , NH_3 , NH_4NO_3 , organic nitrates (RO_xNO_2), and organic nitrogen (C-N bonds)
- the extent to which N is removed during transport along the western slopes of the Sierra in each season
- the characteristics of N in the regional background
- the amount of N emitted by the forests of the Sierra
- the sources of N in rain and snow

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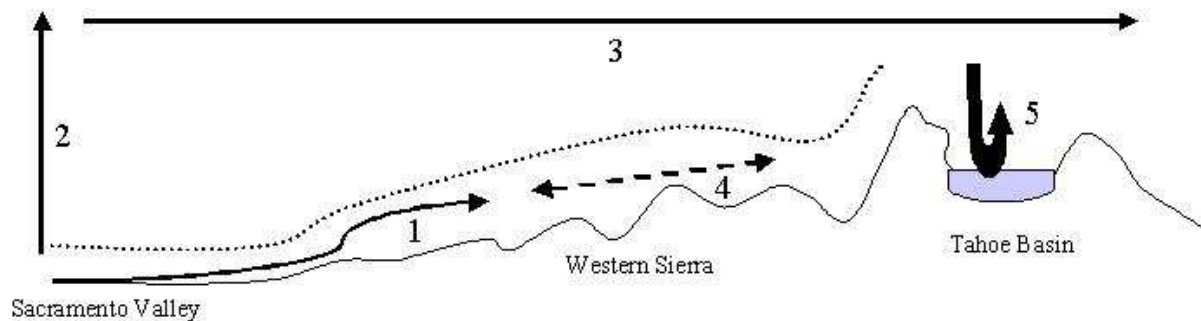


Figure 1. Schematic of possible transport paths between the Central Valley and the Lake Tahoe Basin. The dotted line represents the upper boundary of the mixed or planetary boundary layer. Arrow 1 represents direct transport within the boundary layer, which occurs upslope during the day. Arrow 4 is dotted to represent our uncertainty regarding the easterly extent of this flow on any particular day, or on average. Arrows 2 and 3 show lofting of the air mass above the valley floor and subsequent advection to the east. Arrow 5 represents vertical atmospheric mixing over the lake, which must occur in order for reactive nitrogen that reaches the Basin from the west to impact the lake.

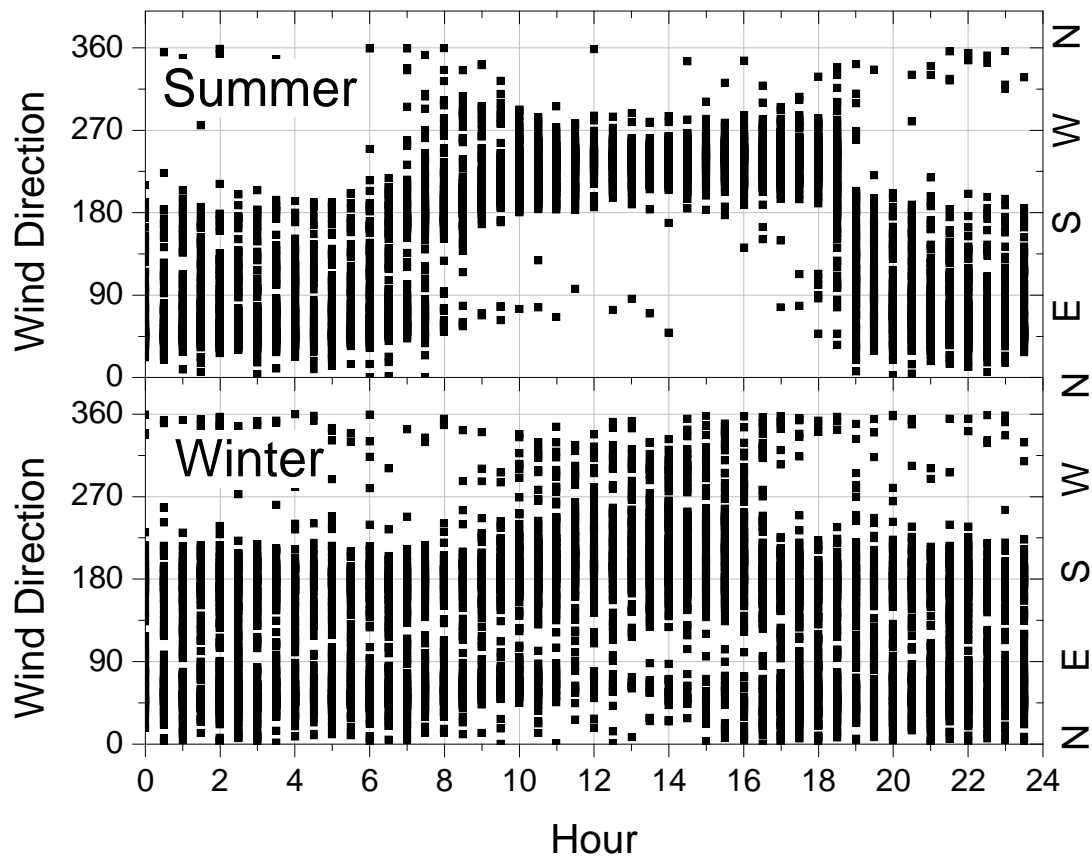


Figure 2. Half hour averages of wind direction observations at Blodgett Forest during 2001. Summer refers to data between day 155 and 255 (June 5- Sep 12) and winter refers to data before day 50 (Feb 20) and after day 300 (Nov 2).

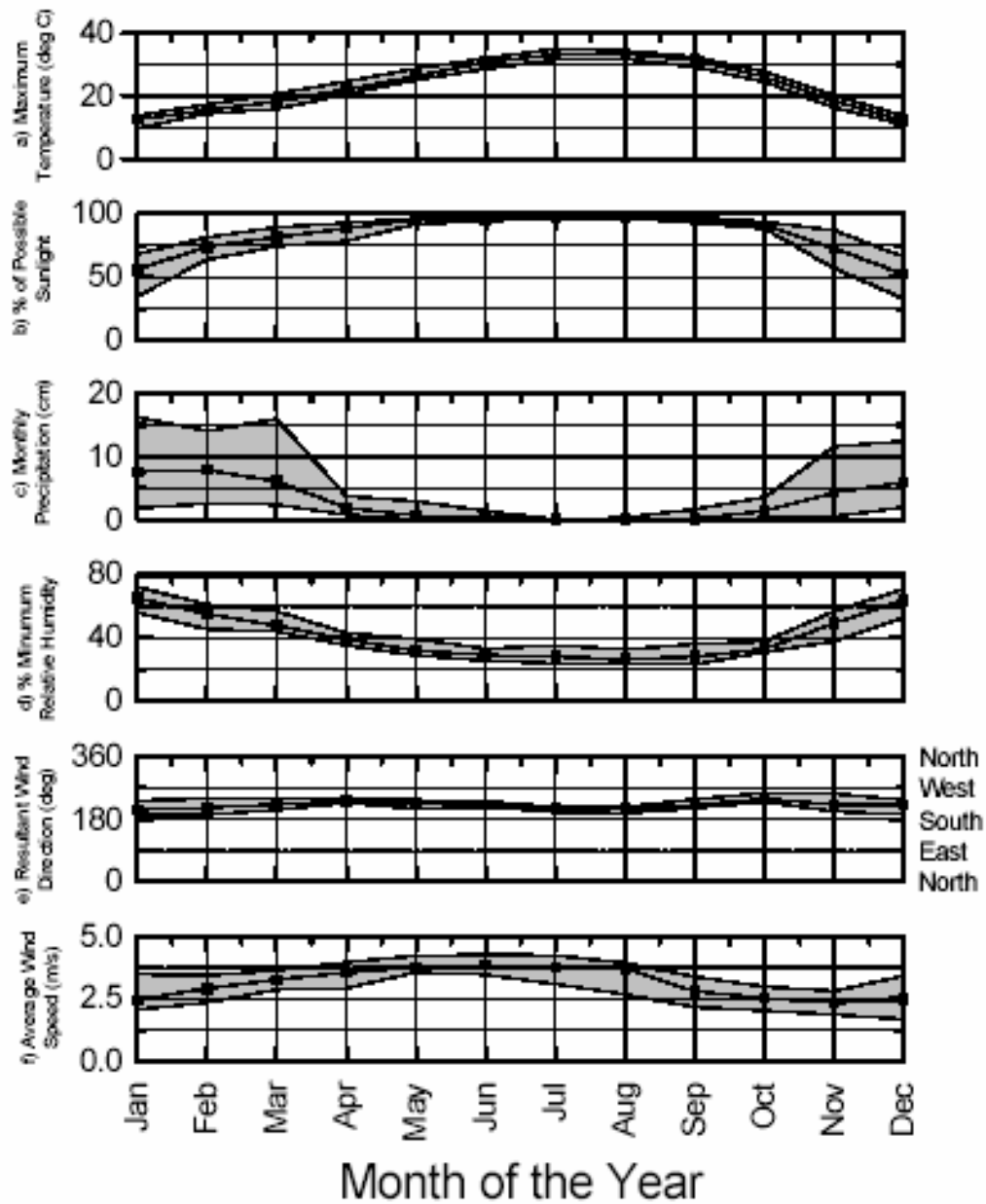


Figure 3. Monthly averaged observations at the Sacramento Executive Airport (WBAN 23232) demonstrate the inter- and intra- annual variance of climatological variables in the region from 1980 through 1999. The line with solid squares is the median of monthly means while the gray swath denotes the 1σ variance. a) maximum daily temperature; b) percent of total possible hours of direct sunlight (no observations were available in 1998 and 1999); c) sum of monthly rainfall; d) the lowest relative humidity recorded each day (typically a late afternoon observation); e) daily origin direction of 24 hour average of recorded winds (also called resultant wind direction); f) 24 hour average of recorded wind speeds.



Figure 4. Major roads and 1998 California Air Resources Board atmospheric sampling sites upwind of the Blodgett Forest Research Station: Photochemical Assessment Monitoring Station sites (circled P), co-located ozone, nitrogen oxide and non-methane hydrocarbon monitors (+), co-located ozone and nitrogen oxide monitors (star), and ozone monitors (diamond). Most observations used in this study were taken from the Blodgett Forest Research Station, Del Paso Manor, and the Folsom sampling sites.

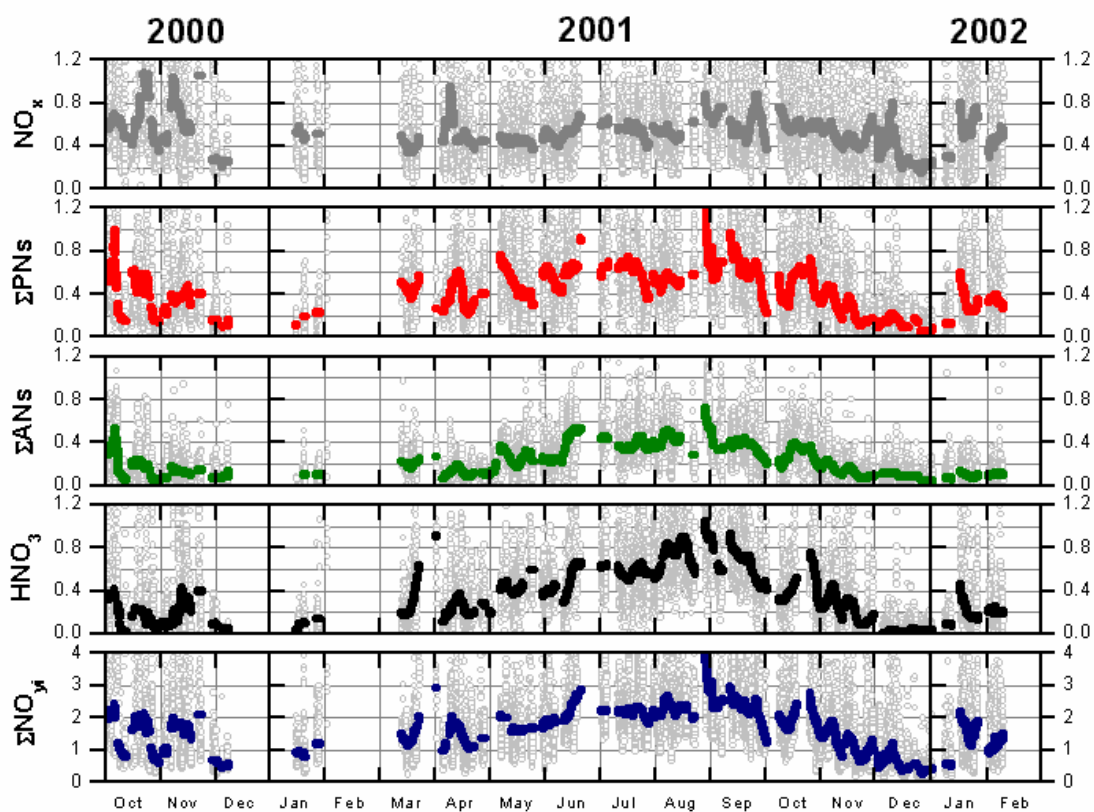


Figure 5. Observations of nitrogen oxides (ppbv) at UC-BFRS 2000-2002 (30-minute averages and 7-day running medians)

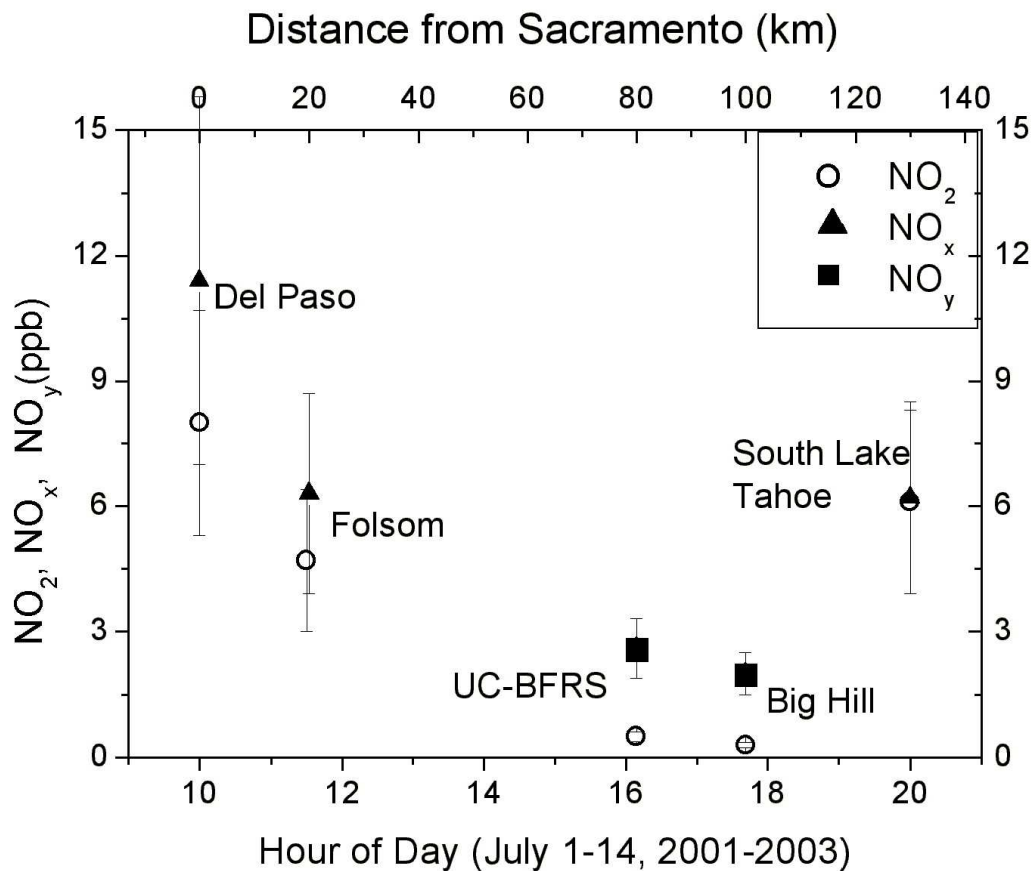


Figure 6. Reactive nitrogen observations along the Sacramento-Tahoe transect. The distance from Sacramento was multiplied by an average wind speed of 3.5 m/s [Dillon 2002] to estimate the time the air mass would arrive at each site after leaving Del Paso at 10 am. Observations at each site were averaged for an hour around the estimated time. For example, UC-BFRS lies 80 km downwind of Del Paso, and NO₂ and NO_y observations between 3 pm and 5 pm were averaged to produce the points reported at 4 pm. The error bars represent the standard deviation of the average.

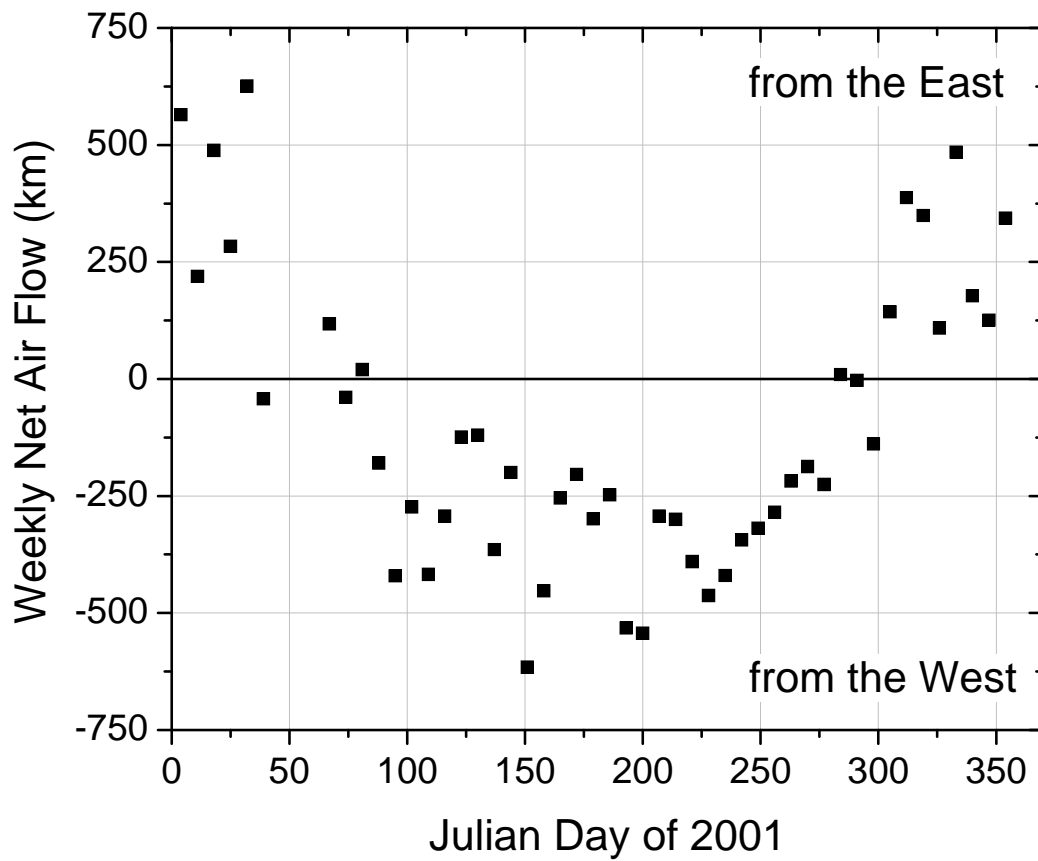


Figure 7. Weekly averages of net east-west air flow throughout 2001 using wind speed and direction data from a 10m tower at Blodgett Forest (1400 m) elevation on the western slope of Sierra Nevada.